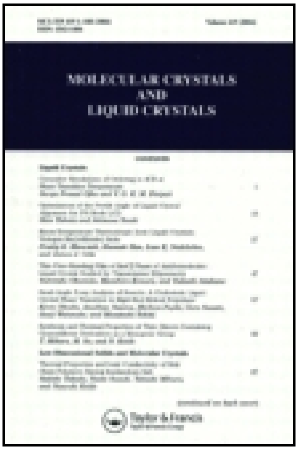

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Computational Approaches to Static Lattice Potential Energy Minimizations for Defects in Organic Molecular Crystals

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Computational Approaches to Static Lattice Potential Energy Minimizations for Defects in Organic Molecular Crystals

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Comparative tests are made of the performance of several methods of minimization in applications to static lattice potential energy calculations made on defects in organic molecular crystals. Tests are made using an earlier reported cyclic procedure based on Newton's method,[1] and an implementation by Powell of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton update[2] applied simultaneously to all variables. The methods and the accuracy attainable by each are described. The results indicate that when not close to a potential energy minimum the methods seem to be equally valuable. However, when close to a potential energy minimum the well-known superior convergence of the BFGS method is exhibited.

1 INTRODUCTION

The solid state computational technique of static lattice potential energy minimization is well-known. Recently this technique has proved to be useful for studying the structure and energetics of defects in organic molecular crystals.[3,4] However, the performance of methods of minimization in applications to this class of problem is not well documented. In contrast, applications to the study of defects in ionic solids are extensive,[5] and there are reports on and comparisons of numerical methods.[6,7] In this work the performance of several methods of minimization is reported in applications to static lattice potential energy calculations made on defects in organic molecular crystals which are assumed to be composed of rigid molecules in their electronic ground state. Comparative tests are made of a cyclic procedure in which one molecule at a time is considered and Newton's method is used,[1] and an implementation by

Powell of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton update formula[2] applied simultaneously to all variables; these methods hereafter are referred to as Methods A and B, respectively. Descriptions of the BFGS update and related quasi-Newton updates can be found in references.[6-12]

The advantages of using Method A are:

(1) that the computer storage requirements are small since only an N-vector (where N is the total number of variables) is needed and this is used to store the displacement variables.

(2) that the C.P.U. time taken in solving the linear algebra required to establish the search direction for the one-molecule problems is small.

(3) that it makes use of first and second derivative information.

The main disadvantage of Method A is that it has a low rate of convergence and the consequences of this will be demonstrated.

The advantages of using Method B are:

(1) that it has a superlinear convergence rate and the consequences of this will be demonstrated.

(2) that it is not too demanding of computer storage, since one $N(N + 13)/2$ matrix[2] is required to store the approximating Hessian and for workspace.

(3) that it makes use of first and second derivative information without the need to re-calculate the latter at the beginning of each iteration.

(4) that the linear algebra is solved efficiently by employing a Cholesky factorization[13] of the Hessian.

(5) that the difficult matter of the line search is managed efficiently.[2]

There are many ways of calculating the structure of defect regions in organic molecular crystals. Symmetry, if present can be used to reduce significantly the computational labor, and schemes can be devised which work efficiently in specific cases by taking account of any other special problem structure. However, the work reported here is directed at developing numerical procedures for defect problems with little or no simplifying structure. Numerical experience alone will ultimately indicate which strategies are the most useful.

2 METHOD

2.1 Problem description

The computational problem has been detailed elsewhere,[4] and is now briefly described. An otherwise perfect crystal contains an arbitrarily large inner region in which the molecules initially occupy a configuration approximately modelling a particular defect of interest. The problem is that of finding the minimal intermolecular potential energy molecular configuration of the defect region subject to the constraint that the molecules of the exterior region of the crystal remain in their experimentally determined perfect crystal positions. Through experience, or trial and error procedures, the size of the region which must be relaxed can be determined. Sometimes this might entail the consideration of hundreds of molecular position and orientation variables.[4]

2.2 The intermolecular potential energy

Tests are to be made on anthracene crystals hence the empirical atom-atom potential method[14] is used with parametrization as in Williams's set IV,[15] and for consistency with the parameter set the carbon-hydrogen bond lengths are taken to be 0.1027 nm. This is the foundation on which the numerical tests to be reported are based.

The calculations employ procedures which are different from those previously reported[4] and they are now discussed. To guarantee function continuity all molecules allowed to relax in the minimization have an environment of molecules with which they interact set at the outset of the calculation. They, i.e. the sets of molecules, remain unchanged and include all molecules whose centers of mass lie within 1.25 nm of the center of mass of the particular defect molecule in the initial molecular configuration. The distance cut-off is problem-dependent and must be chosen to adequately represent the physical situation yet limit computing time requirements. Each molecule-molecule interaction includes all atom-atom interactions. Thus in the course of the numerical work "jumps" in the potential energy caused by molecules or atoms entering or leaving the cut-off radius will not occur. This procedure guards against the failure of the line search. A consequence of the center of mass cut-off is that a number of Hessian matrix elements will be set to zero. Throughout, the quaternion parametrization of the rotation matrix has been used[1,21] and all derivatives of the energy function have been calculated analytically.

2.3 Computational accuracy

All calculations have been performed in double precision arithmetic on a UNIVAC 1100/82 computer for which the maximum allowable precision is 18 significant decimal digits. The dispersion and repulsion contributions to the energy function, gradient of the energy function, and Hessian (matrix of second derivatives) of the energy function have been accumulated separately, with subtractions in the function and derivative expressions being performed at the conclusion of the summation process. The computational accuracy is limited by the loss of 8 significant decimal digits in the calculation of the gradient near the solution point. This has been determined by making a comparison of independently calculated, inversion-related gradient components. Also, in this way some analysis of error growth can be made. It is possible to minimize the energy function up to approximately 10 digit accuracy before round-off errors seriously affect the calculation. The consequences for the convergence in the displacement variables will be considered. The energy function and the molecular displacement variables are reported to more digits than are physically meaningful but this is central to a more complete appreciation of the methods.

2.4 Problems used as examples

It is difficult to find actual problems which exhibit the properties desired for numerical tests. Two relatively simple but instructive examples have been chosen for the purpose of demonstration. The first example is that of a perfect anthracene crystal at 95K[16] and is representative of a molecular configuration close to a potential energy minimum, and the second example is that of a tetracene guest molecule in an anthracene host crystal and is an example of a system "far" from a potential energy minimum in the sense that the gradient norm, i.e. the Euclidean norm of the N-dimensional gradient vector, is large, and the Hessian for the system is not positive definite at the initial molecular configuration point. The latter condition restricts the choice of methods that can be used, *vide infra.*

In each example the twenty molecules nearest the coordinate origin (see Table I of an earlier report[4]) and the origin-centered molecule have been allowed to relax in the minimizations. While these problems are of modest size they serve to demonstrate clearly the differences in performance of the methods studied.

2.5 Methods used

Method A has been described in detail elsewhere.[1] It is a cyclic procedure in which one defect molecule at a time is considered in the minimization and Newton's method is used; the cycling procedure continues until an energy tolerance imposed upon the energy function difference between cycles is not exceeded. The method as used here differs from that previously reported in that the accuracy of the molecular minimizations is determined by a stopping criterion using a constant tolerance[1] ϵ of 10^{-1}, rather than a tolerance which is reduced after each cycle of the minimization. This procedure was adopted to guard against the occurrence of oscillatory behavior in the displacement variables, a possible result of an inexact line search. The value of ϵ was chosen so as not to minimize up to unnecessarily high accuracy or to an accuracy influenced by round-off error. In these tests Method A is penalized. Firstly, it might be possible to avoid inexact line search problems with a larger value of ϵ

than has been used here in the initial cycles, thus requiring fewer function evaluations, and, secondly, the total potential energy has been calculated at the end of each cycle and included in the assessment of performance. In practical applications there is no need for the latter extra computational effort in the first few cycles.

Method B uses an implementation of the BFGS quasi-Newton update formula[2,9] applied simultaneously to all variables. This type of approach has been discussed for the ionic crystals.[6] There are well-known strategies that can be employed at the outset of the calculation. These depend upon the way in which the approximating Hessian is initialized, a concept discussed in the valuable early paper of Fletcher and Powell,[8] and include as possibilities:

(1) initialization to a suitable multiple of the identity matrix.

(2) initialization to the exact Hessian, if it is positive definite. This is highly desirable, *vide infra.*

(3) initialization to that sub-matrix of the exact Hessian which is positive definite with the remaining matrix elements initialized to a suitable multiple of the identity matrix, e.g. consider the ideal case of a guest molecule in a host crystal in which the Hessian of the total intermolecular potential energy has a principal direction of negative curvature associated mainly with a single guest displacement variable ξ. In this case, the approximating Hessian could be initialized to the exact Hessian except for the row and/or column connecting ξ with all other variables, those matrix entries being set to zero except for the diagonal entry which would be set to a positive real number of realistic magnitude. While very useful, this method presupposes some knowledge of the problem's structure and for that reason is not further considered.

Method B(1) has the advantage that it can be applied directly to problems and only the energy function and gradient of the energy function are required to be calculated. The approximating Hessian is built up by so-called rank 2 matrix additions using gradient information.[9] Since the functions dealt with in practice are almost certainly non-quadratic, except near the solution point, the approximating Hessian might need to be re-initialized periodically and this has been done. Method B(1a) will refer to a procedure without periodic re-initialization, and Method B(1b) will refer to a procedure with periodic re-initialization. The number of function/gradient evaluations after which the re-initialization was performed was taken to be fifteen. This number was thought to allow reasonable "downhill" progress to be made without spending excessive computing time searching in non-optimum directions.

If the Hessian is positive definite at some initial configuration point Method B(2) can be used, since this is a requirement of quasi-Newton updates.[12] It is a simple matter to add a sufficiently large multiple of the identity matrix to the exact Hessian to enforce positive definiteness. This procedure was tried and was found to lead to very poor performance and thus was discarded. Numerical experience indicates that in many defect situations the Hessian at the initial molecular configuration point is not likely to be positive definite. Therefore it is necessary to have a fast method for determining whether or not the Hessian of the total intermolecular potential energy is positive definite. From Table II it can be seen that the calculation of the Hessian self-term blocks does not require much C.P.U. time, although even if these blocks are positive definite it does not mean that the full Hessian is positive definite. One fast way of testing for positive definiteness is to perform a Cholesky factorization[13] which requires 5 or 6 seconds of C.P.U. time for the problems considered here (see Table II).

To a certain extent the results of numerical tests can be expected to depend on particular computer subroutine implementations and perhaps on the initial conditions of the problem, e.g. on the initial estimate of step length. Therefore, only results thought likely to be independent of such matters are reported. In this work step length estimates of 10^{-2}–10^{-3} (in units of nm and dimensionless quaternion parameters) were found to be useful initial estimates for each displacement variable.

3 RESULTS

3.1 A perfect anthracene crystal

The atom-atom potential method cannot be expected to calculate crystal structures exactly. For example, if a calculation is made for anthracene at 95K,[16] treating the perfect crystal as if the origin-centered anthracene molecule was a guest molecule, departures from the experimentally determined molecular positions would be expected to occur, and are found. It is usual to find, particularly for crystals of the aromatic hydrocarbons, changes of at most 10^{-3} nm in a center of mass position coordinate and 2°–3° in a principal inertial axis direction angle.[4] These small changes in molecular position and orientation produce, correspondingly, small changes in the molecular interaction energies, which, however, when summed over tens of molecules lead to energy differences which are physically significant, e.g. note that 12.9 kJ mol^{-1} reduction in the energy function listed in Table I. Therefore, it is necessary to allow the same region of the perfect crystal to relax before making a comparison with the analogous total intermolecular potential calculated for the defect crystal. In this way error cancellation can be expected.

Three of the methods were applied to a perfect anthracene crystal. Listed in Table I is the reduction in the total intermolecular potential energy achieved by each method after the indicated number of function/gradient evaluations. Estimates of the C.P.U. time taken in the various types of calculation for this problem are given in Table II and have been used to place the entries in Table I

TABLE I

Reduction in the total intermolecular potential energy for Anthracene achieved by Methods A and B

No. of V, ∇V[a]	Method A[d]		Method B(1a)		Method B(2)	
	V[b]	$\|\nabla V\|$[c]	V	$\|\nabla V\|$	V	$\|\nabla V\|$
1	−3198.7	295.	−3198.7	295.	−3198.7	295.
2					−3211.5	53.
4			−3208.8	189.	−3211.63669	1.
5					−3211.636750	.2
6			−3210.6	187.	−3211.636752	.02
7						
8			−3211.1	104.		
10			−3211.39	63.		
11			−3211.49	104.		
12			−3211.561	48.		
13			−3211.586	53.		
14	−3211.18	97.	−3211.614	27.		
15			−3211.624	29.		
17			−3211.629	15.		
18			−3211.634	11.		
19	−3211.59	36.				
23	−3211.628	15.	Time (min) ≈ 40.			
27	−3211.634	8.				
37			−3211.636752	.1		
Time (min)	≈60.		≈80.		≈18.	

[a] $V \equiv$ total intermolecular potential energy; ∇V is the gradient vector of V.

[b] V is expressed in kJ (mol of system)$^{-1}$.

[c] ∇V is expressed in kJ mol^{-1} nm^{-1} or kJ mol^{-1} per unit quaternion displacement; $\|.\|$ denotes the Euclidean norm.

[d] these results include the time taken to calculate the energy function at the completion of each cycle.

TABLE II

Approximate CPU time used for the anthracene calculations

Calculation[a]	CPU time (mins)[b]
V, ∇V,	2.2
V, ∇V, $\nabla^2 V_i$	3.1
V, ∇V, $\nabla^2 V$	4.6
V, ∇V, $\nabla^2 V$, LDL^T	4.7

[a] $V \equiv$ total intermolecular potential energy.
$\nabla V \equiv$ gradient of V.
$\nabla^2 V_i \equiv$ molecular Hessians.
$\nabla^2 V \equiv$ full Hessian.
$LDL^T \equiv$ Cholesky factorization[13] of $\nabla^2 V$.

[b] Calculations were performed on a UNIVAC 1100/82 computer using double precision arithmetic.

TABLE III

Example of displacement variable[a] convergence taken from the anthracene calculations

Method A		Method B(1a)		Method B(2)	
no. of $V, \nabla V$	ζ	no. of $V, \nabla V$	ζ	no. of $V, \nabla V$	ζ
0	0.	0	0.	0	0.
14	0.0170	4	0.0100	2	0.01806
19	0.0163	6	0.0142	3	0.01476
23	0.01589	8	0.0157	4	0.01555
27	0.01569	10	0.0163	5	0.015521
		11	0.0167	6	0.015520
exact[b]	0.015520	12	0.0166		
		13	0.0162		
		14	0.0160		
		15	0.01581		
		17	0.01576		
		18	0.01575		
		37	0.015528		
		exact	0.015520		

[a] The example shown is that of the quaternion parameter ζ^1 for the origin-centered anthracene molecule.

[b] as calculated by Method B(2).

for Method A. Since the initial molecular configuration point is close to the solution point Method B(1b) is not considered. Table III gives an example, which is representative of the methods used, showing the convergence in a displacement variable.

Analysis of Tables I and III shows that:

(1) the BFGS algorithm with the approximating Hessian initialized to the exact Hessian is the superior method. Little computational effort, after the initial calculation and factorization of the Hessian, is required to minimize the energy function up to 8 digit accuracy and the displacement variables to an accuracy of 4 decimal places. The final total gradient norm implies an average gradient component of 2×10^{-3} kJ mol^{-1}nm^{-1} or 2×10^{-3} kJ mol^{-1} per unit quaternion displacement.

(2) the order of superiority of the methods is Method B(2) > Method B(1a) > Method A, as should be expected on theoretical grounds for a molecular configuration near a solution point.

(3) the termination of any of the minimizations immediately after the energy function has converged in the smallest physically significant digit (here, taken to be the units column) results in two decimal place accuracy in the displacement variables.

(4) the error growth that might be expected for Method B(1a) did not in-

hibit the attainment of the same accuracy in the energy function as achieved by Method B(2), although significantly more function evaluations were required. This does not mean that it will not be a problem in other examples.

(5) there is some oscillatory behavior in the displacement variables for Method B. This occurs because an exact line search is not performed.[2] Monotonic convergence is found for Method A.

3.2 A tetracene guest molecule in an anthracene host crystal

A tetracene molecule, whose atomic position coordinates were taken from Robertson *et al*,[17] was put into the 95K anthracene crystal at the origin-centered site. The tetracene molecular Hessian was found not to be positive definite, so Newton's method was used to find a potential energy minimum for the tetracene in the rigid anthracene host crystal. Subsequently, it was found that the Hessian for the larger problem, i.e. for the tetracene and twenty nearest neighbors, was not positive definite. Therefore, it was not possible to use Method B(2).

Table IV lists the reduction in the total intermolecular potential energy and gradient norm achieved after the indicated number of function/gradient evaluations for Methods A, B(1a) and B(1b). Table V gives an example of the convergence of a displacement variable. The principal findings are:

TABLE IV

Reduction in the total intermolecular potential energy for the tetracene/anthracene system achieved by Methods A and B

No. of	Method A		Method B(1a)		Method B(1b)[c]	
V, ∇V[a]	V	$\lVert\nabla V\rVert$	V	$\lVert\nabla V\rVert$	V	$\lVert\nabla V\rVert$
1	−944.	51653.	−944.	51653.	−944.	51653.
13	−3181.1	228.	−3100.	1888.	−3100.	1888.
18[b]	−3183.1	102.	−3122.	1981.	—	—
23	−3183.47	52.	−3152.	881.	−3179.2	286.
27	−3183.57	28.	−3166.	684.	−3183.0	86.
31	−3183.60	16.	−3167.	622.	−3183.5	40.
35	−3183.6126	9.	−3176.	344.	—	—
50	—	—	−3182.	173.	—	—
	Restart with Method B(2)					
+3	−3183.61697	0.04				

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[a] For definitions of symbols and units used see footnotes to Table I. [CPU time for this example is very nearly the same as that found for perfect anthracene].

[b] CPU time at this stage of the calculation ≈ 40 min.

[c] In these calculations re-initialization of the approximating Hessian was performed after 15 function evaluations.

TABLE V

Example of displacement variable[a] convergence taken from the tetracene/anthracene calculations

no. of $V, \nabla V$	Method A ζ	Method B(1b) ζ
0	0.	0.
13	0.0314	−.0340
18	0.0298	−.0257
23	0.0286	0.0097
27	0.0278	0.0273
31	0.0274	0.0268
35	0.0271	—
exact[b]	0.0267	0.0267

[a] ζ displacement variable[1] for the tetracene guest.
[b] value as calculated by Method B(2) at conclusion of the Method A calculation.

(1) Method A rapidly lowers the function value. The equivalent of thirteen function/gradient evaluations are required to move the system close to the solution point after which, however, the usual low rate of convergence is observed. Table V shows that this method can be expected to achieve two decimal place accuracy in the displacement variables even though five digit accuracy in the energy function has been achieved. At the completion of the Method A calculation Method B(2) was used to finish off. After the calculation and factorization of the Hessian only three function/gradient evaluations were necessary to achieve a final total gradient norm of magnitude similar to that of the anthracene calculation.

(2) Method B(1a) does not perform very well. However, Method B(1b), i.e. with the periodic re-initialization of the approximating Hessian, is significantly better and while it seems that it does not perform quite as well as Method A in the initial stage of the calculation it is overall apparently much the same, with convergence to the solution point expected to be much better.

In recent work performed on excited molecules in crystals[18] displacements in molecular positions of 0.1 nm have been found. In those examples Methods A and B(1b) were found to take more time but the relative performance still seems to remain essentially the same as that reported here.

Since on quadratic functions quasi-Newton methods and conjugate gradient methods generate similar sequences of points,[20] it seems likely that the performance of a conjugate gradient method might be similar to that of Methods B(1a) and B(1b). This was not tested.

4 CONCLUSIONS

Several computational approaches to the problem of static lattice potential energy minimization for defects in organic molecular crystals have been considered. The principal findings are:

(1) that if the initial molecular configuration is thought to be close to a potential energy minimum, and thus the Hessian of the total intermolecular potential energy is expected to be positive definite, the application of a quasi-Newton method, e.g. the BFGS update, to all variables simultaneously with initialization of the approximating Hessian to the exact Hessian is very likely to result in fast convergence to the solution point.

(2) that if the initial molecular configuration is not close to a potential energy minimum the cyclic procedure[1] or a quasi-Newton method using periodic re-initialization of the approximating Hessian are useful ways of first moving the system near to a solution point from where the above recommendation can be implemented to achieve fast convergence. A similar philosophy has been used in other crystal packing calculations.[19]

Addition of molecules to the region of relaxation will not increase the number of significant digits lost in the calculation of the molecular gradients. Therefore, the quality of the results obtained by each of the methods described should, for larger problems, be similar to what is reported here. It is important to ensure convergence to high accuracy, since failure to do so could result in premature termination. In recent calculations a situation arose using Method B(1b) in which some twenty to thirty function/gradient evaluations reduced the energy function by less than 1 kJ mol^{-1} but subsequently large reductions in the energy function occurred.

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APPENDIX

In addition to the expressions given in reference[1] for the calculation of the molecular gradient vector and molecular Hessian, the cross-terms of the Hessian connecting two molecules *i* and *j* are required. The notation of an earlier report[1] is used. The 7 × 7 off-diagonal blocks are calculated using

$$\nabla^2 V_{ij} = -\sum_l \begin{bmatrix} I \\ Q_l \end{bmatrix} \sum_k (\mathrm{V}'_{\mathbf{lk}} I + \mathrm{V}''_{\mathbf{lk}} \mathbf{S}_{\mathbf{lk}} \mathbf{S}^{\mathbf{T}}_{\mathbf{lk}}) \begin{bmatrix} I \\ Q_k \end{bmatrix}^{\mathrm{T}}$$

with

$$Q_k = \nabla^{\mathbf{j}}_{\mathbf{q}}[\mathbf{x}^{\mathbf{T}}_{\mathbf{k}} A^j(q)],$$

where $\nabla^{\mathbf{j}}_{\mathbf{q}}$ indicates that the first partial derivatives are to be taken with respect to the quaternion parameters of molecule j, and $A^j(q)$ is the rotation matrix for molecule j.

References

1. A. O. Griewank, B. R. Markey and D. J. Evans, *J. Chem. Phys.*, **71**, 3449 (1979).
2. M. J. D. Powell, Harwell Subroutine Library, Subroutine VA13A(D), 1975.
3. S. Ramdas and J. M. Thomas in: *Chemical Physics of Solids and Their Surfaces*, Specialist Periodical Reports, **7**, 31 (1978) and references therein.
4. D. P. Craig, A. O. Griewank and B. R. Markey, *Chem. Phys. Lett.*, **62**, 223 (1979).
5. Computer Simulation in the Physics and Chemistry of Solids, S.R.C. Daresbury Laboratory Report DL/SCI/R15, Daresbury, Warrington, U.K.
6. M. J. Norgett and R. Fletcher, *J. Phys. C*, **3**, L190 (1970).
7. A. B. Lidiard and M. J. Norgett, in: *Computational Solid State Physics*, eds. F. Herman, N. W. Dalton and T. R. Koehler (Plenum Press, New York-London, 1972) 385.
8. R. Fletcher and M. J. D. Powell, *Comp. J.*, **6**, 163 (1963).
9. R. Fletcher, *Comp. J.*, **13**, 317 (1970).
10. C. G. Broyden, *J. Inst. Maths. Applics.*, **6**, 76 (1970).
11. C. G. Broyden, *J. Inst. Maths. Applics.*, **6**, 222 (1970).
12. J. E. Dennis and J. J. Moré, *SIAM Review*, **19**, 46 (1977) and references therein.
13. R. S. Martin, G. Peters and J. H. Wilkinson, in: *Handbook for Automatic Computation*, Vol. **2**: Linear Algebra, eds. J. H. Wilkinson and C. Reinsch (Springer, Berlin, 1971) 9.
14. A. I. Kitaigorodsky, *Molecular Crystals and Molecules* (Academic Press, New York, 1973).
15. D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).
16. R. Mason, *Acta Cryst.*, **17**, 547 (1964).
17. J. M. Robertson, V. C. Sinclair and J. Trotter, *Acta Cryst.*, **14**, 697 (1961).
18. D. P. Craig and C. P. Mallett, *Chem. Phys.* (in press).
19. E. Huler and A. Warshel, *Acta Cryst.*, **B30**, 1822 (1974).
20. G. R. Walsh, *Methods of Optimization* (J. Wiley and Sons, London, 1977).
21. H. Goldstein, *Classical Mechanics*, 2nd Edition (Addison-Wesley, Reading, 1980).